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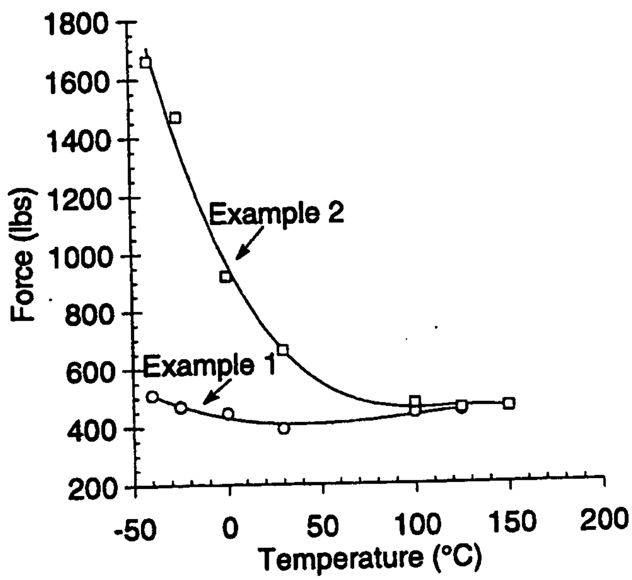

(57) Abstract

A magnetorheological material containing a particle component and a carrier fluid having a change in viscosity per degree temperature ($\Delta\eta/\Delta T$ ratio) less than or equal to about 9.0 centipoise/°C over the temperature range of 25 °C to -40 °C. The magnetorheological material exhibits a substantial magnetorheological effect with a minimal variation in mechanical properties with respect to changes in temperature. The magnetorheological material is advantageous in that it provides for the design of devices that are smaller, more efficient and consume less power.

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Description

LOW VISCOSITY MAGNETORHEOLOGICAL MATERIALS

Technical Field

The present invention relates to certain fluid materials which exhibit substantial increases in flow resistance when exposed to magnetic fields. More specifically, the present invention relates to low viscosity magnetorheological materials that substantially minimize the variance in force required by a magnetorheological device over a given temperature range.

Background Art

Fluid compositions which undergo a change in apparent viscosity in the presence of a magnetic field are commonly referred to as Bingham magnetic fluids or magnetorheological materials. Magnetorheological materials normally are comprised of ferromagnetic or paramagnetic particles, typically greater than 0.1 micrometers in diameter, dispersed within a carrier fluid and in the presence of a magnetic field, the particles become polarized and are thereby organized into chains of particles within the fluid. The chains of particles act to increase the apparent viscosity or flow resistance of the overall material and in the absence of a magnetic field, the particles return to an unorganized or free state and the apparent viscosity or flow resistance of the overall material is correspondingly reduced. These Bingham magnetic fluid compositions exhibit controllable behavior similar to that commonly observed for electrorheological materials, which are responsive to an electric field instead of a magnetic field.

Both electrorheological and magnetorheological materials are useful in providing varying damping forces within devices, such as dampers, shock absorbers and elastomeric mounts, as well as in controlling torque and or pressure levels in various clutch, brake and valve devices. Magnetorheological materials inherently offer several advantages over electrorheological materials in these applications.

Magnetorheological fluids exhibit higher yield strengths than electrorheological materials and are, therefore, capable of generating greater damping forces. Furthermore, magnetorheological materials are activated by magnetic fields which are easily produced by simple, low voltage electromagnetic coils as compared to the expensive high voltage power supplies required to effectively operate electrorheological materials. A more specific description of the type of devices in which magnetorheological materials can be effectively utilized is provided in co-pending U.S. Patent Application Serial Nos. 07/900,571 and 07/900,567 entitled "Magnetorheological Fluid Dampers" and "Magnetorheological Fluid Devices," respectively, both filed on June 18, 1992, the entire contents of which are incorporated herein by reference.

Magnetorheological or Bingham magnetic fluids are distinguishable from colloidal magnetic fluids or ferrofluids. In colloidal magnetic fluids the particles are typically 5 to 10 nanometers in diameter. Upon the application of a magnetic field, a colloidal ferrofluid does not exhibit particle structuring or the development of a resistance to flow. Instead, colloidal magnetic fluids experience a body force on the entire material that is proportional to the magnetic field gradient. This force causes the entire colloidal ferrofluid to be attracted to regions of high magnetic field strength.

Magnetorheological fluids and corresponding devices have been discussed in various patents and publications. For example, U.S. Pat. No. 2,575,360 provides a description of an electromechanically controllable torque-applying device that uses a magnetorheological material to provide a drive connection between two independently rotating components, such as those found in clutches and brakes. A fluid composition satisfactory for this application is stated to consist of 50% by volume of a soft iron dust, commonly referred to as "carbonyl iron powder", dispersed in a suitable liquid medium such as a light lubricating oil.

Another apparatus capable of controlling the slippage between moving parts through the use of magnetic or electric fields is disclosed in U.S. Pat. No. 2,661,825. The space between the moveable parts is

filled with a field responsive medium. The development of a magnetic or electric field flux through this medium results in control of resulting slippage. A fluid responsive to the application of a magnetic field is described to contain carbonyl iron powder and light weight mineral oil.

U.S. Pat. No. 2,886,151 describes force transmitting devices, such as clutches and brakes, that utilize a fluid film coupling responsive to either electric or magnetic fields. An example of a magnetic field responsive fluid is disclosed to contain reduced iron oxide powder and a lubricant grade oil having a viscosity of from 2 to 20 centipoises at 25°C.

The construction of valves useful for controlling the flow of magnetorheological fluids is described in U.S. Pat. Nos. 2,670,749 and 3,010,471. The magnetic fluids applicable for utilization in the disclosed valve designs include ferromagnetic, paramagnetic and diamagnetic materials. A specific magnetic fluid composition specified in U.S. Pat. No. 3,010,471 consists of a suspension of carbonyl iron in a light weight hydrocarbon oil. Magnetic fluid mixtures useful in U.S. Pat. No. 2,670,749 are described to consist of a carbonyl iron powder dispersed in either a silicone oil or a chlorinated or fluorinated suspension fluid.

Various magnetorheological material mixtures are disclosed in U.S. Pat. No. 2,667,237. The mixture is defined as a dispersion of small paramagnetic or ferromagnetic particles in either a liquid, coolant, antioxidant gas or a semi-solid grease. A preferred composition for a magnetorheological material consists of iron powder and light machine oil. A specifically preferred magnetic powder is stated to be carbonyl iron powder with an average particle size of 8 micrometers. Other possible carrier components include kerosene, grease, and silicone oil.

U.S. Pat. No. 4,992,190 discloses a rheological material that is responsive to a magnetic field. The composition of this material is disclosed to be magnetizable particles and silica gel dispersed in a liquid carrier vehicle. The magnetizable particles can be powdered

magnetite or carbonyl iron powders with insulated reduced carbonyl iron powder, such as that manufactured by GAF Corporation, being specifically preferred. The liquid carrier vehicle is described as having a viscosity in the range of 1 to 1000 centipoises at 100°F. Specific examples of suitable vehicles include Conoco LVT oil, kerosene, light paraffin oil, mineral oil, and silicone oil. A preferred carrier vehicle is silicone oil having a viscosity in the range of about 10 to 1000 centipoise at 100°F.

It is desirable that the continous component or carrier fluid of a magnetorheological material exhibit several basic characteristics. These characteristics include: (a) chemical compatibility with both the particle component of the fluid and device materials; (b) relatively low cost; (c) low thermal expansion; and (d) high density. Magnetorheological materials should also be non-hazardous to the surrounding environment and, more importantly, be capable of functioning consistently over a broad temperature range.

Most of the carrier fluid components that are traditionally used in magnetorheological materials as previously described cannot adequately meet all of these basic requirements. For instance, many of the previously described magnetorheological materials cause large variations in the force exhibited by a magnetorheological device utilizing the materials over a broad temperature range. Hence, many of the magnetorheological materials prepared with traditional carrier fluids cannot be effectively utilized in automotive and aerospace damping devices and the like which require consistent application of precisely controlled force over widely varying temperatures.

Characterization of the performance of magnetorheological materials with respect to a change in operating temperature is vital to the successful commercialization of most magnetorheological devices, such as clutches, brakes, dampers, shock absorbers and engine mounts. All of these devices inherently experience a variation in operating temperature over their lifetime. For instance, specifications for automotive and aerospace applications typically require the device to operate at or survive exposure to temperatures ranging from about -40°C to 150°C.

A need therefore exists for magnetorheological materials that exhibit limited variation in properties over a broad temperature range.

Disclosure of Invention

The present invention is a magnetorheological material which exhibits a substantial magnetorheological effect with a minimal variation in mechanical properties with respect to changes in temperature. More specifically, the present invention comprises a carrier fluid and a particle component wherein the carrier fluid has a change in viscosity (η) per degree temperature (T) ($\Delta\eta/\Delta T$ ratio) less than or equal to about 9.0 centipoise/°C over the temperature range of 25°C to -40°C.

It has presently been discovered that carrier fluids having a $\Delta\eta/\Delta T$ ratio less than or equal to about 9.0 centipoise/°C over the temperature range of 25 to -40°C can be utilized to prepare magnetorheological materials which have an unusually low variance of mechanical properties over a broad temperature range. Conventional carrier fluids, such as mineral oils and paraffin oils typically have a $\Delta\eta/\Delta T$ ratio greater than the limit described above and are therefore unacceptable for utilization over a broad temperature range. Polysiloxanes and perfluorinated polyethers having a viscosity between about 3 and 200 centipoise at 25°C have an appropriate $\Delta\eta/\Delta T$ ratio and can be utilized to prepare especially preferred magnetorheological materials which have unusually low variance of mechanical properties over a broad temperature range. More specifically, the magnetorheological materials of the invention when utilized in a device, such as a damper, mount or clutch, exhibit significantly less variation in the force output over a temperature range from about -40° to 150°C as compared to devices using magnetorheological materials prepared with traditional carrier fluids.

Brief Description of the Drawing

Figure 1 shows the force output for a linear magnetorheological damper plotted as a function of temperature. The force data obtained for this damper at a magnetic field of about 1000 Oersted

using a low viscosity magnetorheological material of the present invention (Example 1) is contrasted against data obtained with this damper under similar conditions using a higher viscosity comparative magnetorheological material (Example 2).

Best Mode for Carrying Out the Invention

The magnetorheological material of the present invention comprises a carrier fluid and a particle component wherein the carrier fluid has a change in viscosity per degree temperature ($\Delta\eta/\Delta T$ ratio) less than or equal to about 9.0 centipoise/°C, preferably less than or equal to about 7.0 centipoise/°C, over the temperature range of 25°C to -40°C.

Examples of carrier fluids having an appropriate ($\Delta\eta/\Delta T$) ratio include propylene glycol, acetic anhydride, allyl isothiocyanate, benzylacetate, bis(2-butoxy ethyl) ether, bis(2-chloroethyl) ether, bis(2-ethoxyethyl) ether, bis-(2-ethylhexyl)-o-phthalate, bis(2-mercaptoethyl) sulfide, bis(2-methoxyethyl) ether, 1-bromoheptane, 1-bromohexane, 1-bromooctane, 1,3-butanediol, 2-(2-butoxyethoxy)ethanol, butylbenzene, butylcyclohexane, N-butyldiethanolamine, butyric anhydride, 1-chloro-2-ethylbenzene, 1-chloro-4-ethylbenzene, 1-chloroheptane, 1-chlorooctane, 3-chloropropionitrile, 3-chlorotoluene, cyclohexanone, cyclohexylacetate, cyclooctylamine, decamethyltetrasiloxane, 1-decene, 1,2-dibromobutane, 1,2-dibromo-1,1-dichloroethane, 1,2-dibutoxyethane, dibutyl disulfide, dibutyl maleate, dibutyl sulfide, 2-diethylaminoethanol, 1,4-diethylbenzene, diethyl bromomalonate, diethylsulfide, di-(2-ethylhexyl)-o-phthalate, diethyl malonate, N,N-dimethylbenzylamine, N,N-dimethylformamide, dimethyl malonate, 2,4-dimethylpyridine, dipropyl disulfide, 2-(2-ethoxyethoxy)ethanol, 2-ethoxyethyl acetate, 2-(ethylamino)ethanol, N-ethylaniline, N-ethyldiethanolamine, 2,2'-(ethylenedioxy)bisethanol, ethyl heptanoate, ethyl hexanoate, 2-ethylhexanoic acid, 2-ethyl-1-hexanol, 2-ethylhexyl acetate, ethyl octanoate, S-ethylthioethanol, ethyltoluene, 4-fluoro-1-methoxybenzene, glyceryl tributyrate, heptacosofluoro-tributylamine, heptanal, 1-heptanethiol, hexafluoro-2-phenyl-2-propanol, cis-hexahydroindane, 2,5-hexanediol, hexanenitrile, 1-hexanetriol, 1-hexanol, hexyl acetate, 2-hydroxyethylhydrazine, 4-hydroxy-4-methyl-

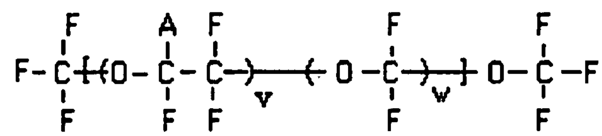
2-pentanone, 3-hydroxypropionitrile, indan, 1-iodoheptane, 1-iodopentane, isobutylbenzene, isopropylbenzene, isopropylcyclohexane, isopropyl-1-methylbenzene, limonene, 3-methoxy-1-butanol, 2-(2-methoxyethoxy)ethanol, methyl acetoacetate, N-methylaniline, methylcyclopentadiene dimer, methyl heptanoate, methyl hexanoate, 1-methylimidazole, 4-methylpentanenitrile, 2-methylpentanoic acid, 2-methylpropionic acid, 1-nitrobutane, 2-nitroethanol, nonane, nonanoyl chloride, octanenitrile, 1-octanethiol, octanoyl chloride, 1,5-pentanediamine, pentyl acetate, 1-phenylhexane, pinane, pinene, 1,2,3-propanetriol triacetate, cis-propenylbenzene, propionic anhydride, propylcyclohexane, propyl benzoate, squalene, tetraethylgermanium, tetraethyltin, tetrahydropyran-2-methanol, 2,6,10,14-tetramethylpentadecane, tributylamine, tributyl borate, tributyl phosphate, 1,3,5-trimethylbenzene, 2,6,8-trimethyl-4-nonanone, trimethylphospate, 1,2,4-trimethylpiperazine, tripropylamine, 1-undecene, and mixtures thereof, as well as mixtures of propylene glycol and ethylene glycol with water wherein the ratio of alkylene glycol to water is between 60:40 to 95:5.

The preferred carrier fluids of the present invention are polysiloxanes and perfluorinated polyethers having a viscosity between about 3 and 200, preferably between about 5 and 100, centipoise at 25°C.

The polysiloxanes of the invention can be any silicone homopolymer or copolymer comprising a siloxane polymeric backbone substituted with hydrocarbon radicals as side and end groups. The hydrocarbon radicals can be either straight chain, branched or cyclic, as well as aliphatic or aromatic with the number of carbon atoms ranging from 1 to about 8. In addition, the hydrocarbon radicals may contain H, N, O, S, Cl, Br and F functionality as in the case of fluorinated polysiloxanes. Examples of commercially available polysiloxanes include polydimethylsiloxanes, polymethylphenylsiloxanes, poly(methyl-3,3,3-trifluoropropyl)siloxanes, polychlorophenylmethylsiloxanes, dimethyl(tetrachlorophenyl)siloxane copolymers, dimethyl(phenylmethyl)siloxane copolymers, dimethyl(diphenyl)siloxane copolymers, and methyl-3,3,3-trifluoropropyl(di-

methyl)siloxane copolymers with polydimethylsiloxanes being preferred.

The perfluorinated polyethers can be any linear fluorinated polymers containing a polyether backbone consisting of carbon and oxygen atoms with either CF_3 or F functionality. The perfluorinated polyethers of the invention correspond to the following formula:



wherein A can be F or CF_3 and the ratio of v/w is between about 30 and 50, preferably between about 35 and 45. Examples of commercially available perfluorinated polyethers include both the GALDEN and FOMBLIN fluorinated liquids available from Montedison USA, Incorporated.

The polysiloxanes and perfluorinated polyethers of the invention may be prepared by methods well known in the art and many are commercially available as described above. The viscosity of commercially available polysiloxanes and perfluorinated polyethers can, if needed, be reduced by techniques well known to those skilled in the art of manufacturing silicone and organosilicon compounds. Such techniques include thermal depolymerization at high temperatures and reduced pressures, as well as both acid and base depolymerization in the presence of an appropriate endblocking agent, such as hexamethyldisiloxane.

Due to their ability to exhibit a somewhat lower temperature dependence on viscosity, the polysiloxanes are preferred over the perfluorinated polyethers for use in the present invention with polydimethylsiloxanes being especially preferred.

The carrier fluid of the invention may also be a mixture of two or more of any of the carrier fluids described above.

The carrier fluid of the present invention is typically utilized in an amount ranging from about 50 to 95, preferably from about 60 to 85,

percent by volume of the total magnetorheological material. This corresponds to about 11 to 70, preferably about 15 to 41, percent by weight when the carrier fluid and particle of the magnetorheological material have a specific gravity of about 0.95 and 7.86, respectively.

It is imperative that the carrier fluids of the invention have a ($\Delta\eta/\Delta T$ ratio) less than or equal to about 9.0 centipoise/°C over the temperature range of 25°C to -40°C, since carrier fluids having a $\Delta\eta/\Delta T$ ratio within this range have been found to impart unexpectedly superior temperature stability to a corresponding magnetorheological material. Specifically, the low viscosity magnetorheological materials of the present invention are capable of exhibiting significantly less variance in mechanical properties over a temperature range of about -40 to 150°C than magnetorheological materials prepared with higher viscosity polysiloxanes, higher viscosity perfluorinated polyethers or conventional carrier components, such as paraffin or mineral oils. Therefore, devices (i.e., dampers, mounts, clutches, etc.) that utilize the magnetorheological materials of the invention exhibit a more constant force output over a broad temperature range than devices utilizing magnetorheological materials prepared with traditional carrier components.

The minimal variation in mechanical properties with respect to a change in temperature of the present magnetorheological materials is advantageous in that it allows for the design of smaller, more efficient devices in most applications. In addition, the low viscosity magnetorheological materials of the invention allow a design engineer greater leeway in the ultimate geometry or shape of a device, as well as in methods to control the power consumption of a device.

The particle component of the magnetorheological material of the invention can be comprised of essentially any solid which is known to exhibit magnetorheological activity. Typical particle components useful in the present invention are comprised of, for example, paramagnetic, superparamagnetic or ferromagnetic compounds. Specific examples of particle components useful in the present invention include particles comprised of materials such as iron, iron oxide, iron nitride, iron carbide, carbonyl iron, chromium dioxide, low

carbon steel, silicon steel, nickel, cobalt, and mixtures thereof. The iron oxide includes all known pure iron oxides, such as Fe_2O_3 and Fe_3O_4, as well as those containing small amounts of other elements, such as manganese, zinc or barium. Specific examples of iron oxide include ferrites and magnetites. In addition, the particle component can be comprised of any of the known alloys of iron, such as those containing aluminum, silicon, cobalt, nickel, vanadium, molybdenum, chromium, tungsten, manganese and/or copper. The particle component can also be comprised of the specific iron-cobalt and iron-nickel alloys described in the U.S. patent application entitled "Magnetorheological Materials Based on Alloy Particles" filed concurrently herewith by Applicants J. D. Carlson and K. D. Weiss and also assigned to the present assignee, the entire disclosure of which is incorporated herein by reference.

The particle component is typically in the form of a metal powder which can be prepared by processes well known to those skilled in the art. Typical methods for the preparation of metal powders include the reduction of metal oxides, grinding or attrition, electrolytic deposition, metal carbonyl decomposition, rapid solidification, or smelt processing. Various metal powders that are commercially available include straight iron powders, reduced iron powders, insulated reduced iron powders, and cobalt powders. The diameter of the particles utilized herein can range from about 0.1 to 500 μm and preferably range from about 1.0 to 50 μm.

The preferred particles of the present invention are straight iron powders, reduced iron powders, iron oxide powder/straight iron powder mixtures and iron oxide powder/reduced iron powder mixtures. The iron oxide powder/iron powder mixtures are advantageous in that the iron oxide powder, upon mixing with the iron powder, is believed to remove any corrosion products from the surface of the iron powder so as to enhance the magnetorheological activity of the overall material. Iron oxide powder/iron powder mixtures are further described in the U.S. patent application entitled "Magnetorheological Materials Utilizing Surface-Modified Particles," filed concurrently herewith by Applicants K.D. Weiss, J. D. Carlson

and D. A. Nixon, and also assigned to the present assignee, the entire disclosure of which is incorporated herein by reference.

The particle component typically comprises from about 5 to 50, preferably about 15 to 40, percent by volume of the total composition depending on the desired magnetic activity and viscosity of the overall material. This corresponds to about 30 to 89, preferably about 59 to 85, percent by weight when the carrier fluid and particle of the magnetorheological material have a specific gravity of about 0.95 and 7.86, respectively.

A surfactant to disperse the particle component may also be optionally utilized in the present invention. Such surfactants include known surfactants or dispersing agents such as ferrous oleate and naphthenate, metallic soaps (e.g., aluminum tristearate and distearate), alkaline soaps (e.g., lithium and sodium stearate), sulfonates, phosphate esters, stearic acid, glycerol monooleate, sorbitan sesquioleate, stearates, laurates, fatty acids, fatty alcohols, and the other surface active agents discussed in U.S. Patent No. 3,047,507 (incorporated herein by reference). In addition, the optional surfactant may be comprised of steric stabilizing molecules, including fluoroaliphatic polymeric esters, such as FC-430 (3M Corporation), and titanate, aluminate or zirconate coupling agents, such as KEN-REACT (Kenrich Petrochemicals, Inc.) coupling agents. The optional surfactant also may be hydrophobic metal oxide powders, such as AEROSIL R972, R974, EPR976, R805 and R812 (Degussa Corporation) and CABOSIL TS-530 and TS-610 (Cabot Corporation) surface-treated hydrophobic fumed silica. Finally, a precipitated silica gel, such as that disclosed in U.S. Patent No. 4,992,190 (incorporated herein by reference), can be used to disperse the particle component. In order to reduce the presence of moisture in the magnetorheological material, it is preferred that the precipitated silica gel dispersant, if utilized, be dried in a convection oven at a temperature of from about 110°C to 150°C for a period of time from about 3 hours to 24 hours.

The surfactant, if utilized, is preferably a hydrophobic fumed silica, a "dried" precipitated silica gel, a phosphate ester, a fluoroaliphatic polymeric ester, or a coupling agent. The optional

surfactant may be employed in an amount ranging from about 0.1 to 20 percent by weight relative to the weight of the particle component.

Particle settling may be minimized in the magnetorheological materials of the present invention by forming a thixotropic network. A thixotropic network is defined as a suspension of particles that, at low shear rates, form a loose network or structure sometimes referred to as clusters or flocculates. The presence of this three-dimensional structure imparts a small degree of rigidity to the magnetorheological material, thereby reducing particle settling. However, when a shearing force is applied through mild agitation, this structure is easily disrupted or dispersed. When the shearing force is removed, this loose network is reformed over a period of time.

A thixotropic network or structure is formed through the utilization of a hydrogen-bonding thixotropic agent and/or a polymer-modified metal oxide. Colloidal additives may also be utilized to assist in the formation of the thixotropic network. The formation of a thixotropic network utilizing hydrogen-bonding thxiotropic agents, polymer-modified metal oxides and colloidal additives is further described in the U.S. Patent Application entitled "Thixotropic Magnetorheological Materials," filed concurrently herewith by applicants K. D. Weiss, D. A. Nixon, J. D. Carlson and A. J. Margida and also assigned to the present assignee, the entire disclosure of which is incorporated herein by reference.

The magnetorheological materials of the present invention can be prepared by initially mixing the ingredients together by hand (low shear) with a spatula or the like and then subsequently more thoroughly mixing (high shear) with a homogenizer, mechanical mixer or shaker or dispersing with an appropriate milling device such as a ball mill, sand mill, attritor mill, paint mill, colloid mill or the like, in order to create a more stable suspension.

Evaluation of the mechanical properties and characteristics of the magnetorheological materials of the present invention, as well as other magnetorheological materials, can be obtained through the use of parallel plate and/or concentric cylinder couette rheometry. The

theories which provide the basis for these techniques are adequately described by S. Oka in *Rheology, Theory and Applications* (volume 3, F. R. Eirich, ed., Academic Press: New York, 1960) the entire contents of which are incorporated herein by reference. The information that can be obtained from a rheometer includes data relating mechanical shear stress as a function of shear strain rate. For magneto-rheological materials, the shear stress versus shear strain rate data can be modeled after a Bingham plastic in order to determine the dynamic yield stress and viscosity. Within the confines of this model the dynamic yield stress for the magnetorheological material corresponds to the zero-rate intercept of a linear regression curve fit to the measured data. The magnetorheological effect at a particular magnetic field can be further defined as the difference between the dynamic yield stress measured at that magnetic field and the dynamic yield stress measured when no magnetic field is present.

In a concentric cylinder cell configuration the magneto-rheological material is placed in the annular gap formed between an inner cylinder of radius R_1 and an outer cylinder of radius R_2, while in a simple parallel plate configuration the material is placed in the planar gap formed between upper and lower plates both with a radius, R_3. In these techniques either one of the plates or cylinders is then rotated with an angular velocity ω while the other plate or cylinder is held motionless. A magnetic field is typically applied to these cell configurations across the fluid-filled gap, either radially for the concentric cylinder configuration, or axially for the parallel plate configuration. The relationship between the shear stress and the shear strain rate is then derived from this angular velocity and the torque, T, applied to maintain or resist it.

The testing of various application specific devices, such as dampers, mounts and clutches, that utilize either the magneto-rheological materials of the present invention or other magneto-rheological materials, is a second method of evaluating the mechanical performance of these materials. The magnetorheological material-containing device is simply placed in line with a mechanical actuator and operated with a specified displacement amplitude and

frequency. A magnetic field is appropriately applied to the device and the force output determined from the resulting extension/compression waveforms plotted as a function of time. The methodology utilized to test dampers, mounts and clutches is well known to those skilled in the art of vibration control.

The following examples are given to illustrate the invention and should not be construed to limit the scope of the invention. In the examples, all viscosities are stated as being measured at 25°C and are given in centipoise.

Example 1

A magnetorheological material is prepared by adding together a total of 1257.6 g straight carbonyl iron powder (MICROPOWDER-S-1640, which is similar to old E1 iron powder notation, from GAF Chemicals Corporation), 25.0 g Mn/Zn ferrite (#73302-0, D. M. Steward Manufacturing Company), 17.3 g siloxane oligomer-modified silica (CABOSIL TS-720, Cabot Corporation) as a polymer-modified metal oxide, and 25.2 g of a phosphate ester dispersant (EMPHOS CS-141, Witco Chemical Corporation) with 294.7 g polydimethylsiloxane oil (L-45, 10 centistoke, Union Carbide Chemicals and Plastics Company, Inc.). The viscosity of the polydimethylsiloxane is measured by concentric cylinder rheometry to be about 16 centipoise. The magnetorheological material is made into a homogeneous mixture over a 16-hour period using an attritor mill. The material is stored in a polyethylene container until utilized.

Comparative Example 2

A magnetorheological material is prepared according to the procedure described in Example 1. However, in this example the 16 centipoise polydimethylsiloxane oil is replaced with a higher viscosity silicone oil (PS042, 500 centistoke, Hüls America Inc.). The viscosity of this silicone oil is measured by concentric cylinder rheometry to be about 660 centipoise. The magnetorheological material is stored in a polyethylene container until utilized.

Mechanical Properties of Examples 1 and 2

The mechanical performance of the magnetorheological materials prepared in Examples 1 and 2 are evaluated in a linear magnetorheological damper over a temperature range of -40 to 150°C. More specifically, this damper contains approximately 250 mL of a magnetorheological material that is forced to flow by the movement of a piston. A magnetic field is generated and controlled across a gap within the device through the application of electric current to an electromagnetic coil contained within the piston. The width of this gap through which the fluid flows is about 1.5 mm. During the tests the damper is operated at a frequency of 1.0 Hz with a displacement amplitude of ± 0.5 inch. A magnetic field is appropriately applied to the device and the force output determined from the resulting extension/compression waveforms plotted as a function of time.

The force output of this linear damper utilizing a low viscosity magnetorheological material of the present invention (Example 1) is compared in Figure 1 to the force output of this same damper using a high viscosity comparative magnetorheological material (Example 2). In this figure the measured force data at a magnetic field of about 1000 Oersted is plotted as a function of temperature. The damper utilizing a magnetorheological material of the invention is observed to provide a relatively constant (less than about 15% variation) force output over the temperature range of -40 to 150°C, while the force output of this same damper varies by greater than about 70% over this temperature range when the comparative magnetorheological material of Example 2 is utilized.

Viscosity Reduction of Fluorinated Polysiloxanes

To a reaction flask equipped with a magnetic stir bar is added 500 mL of a poly(methyl-3,3,3-trifluoropropyl)siloxane (PS181, 300 centistoke, Huls America Inc.), 108 g of concentrated sulfuric acid (Aldrich Chemical Co.) and 51.0 g hexamethyldisiloxane (99.95%, Aldrich Chemical Co.). The reaction flask is then fitted with a drying tube. The reaction mixture is stirred for five days at room

temperature. A total of 100 mL of distilled deionized water is added to the reaction mixture. After stirring for two hours, the organic layer is removed and washed three times with 100 mL portions of distilled deionized water, four times with 40 mL portions of 10% sodium bicarbonate solution and seven times with 100 mL portions of distilled deionized water. Any excess hexamethyldisiloxane is removed under reduced pressure at 60°C. The remaining poly(methyl-3,3,3-trifluoropropyl)siloxane is characterized by infrared spectroscopy and ^{13}C nuclear magnetic resonance spectroscopy and the viscosity is measured using concentric cylinder rheometry to be about 83 centipoise (66 centistoke). This low viscosity fluorinated polysiloxane is stored in a polyethylene bottle until utilized.

Examples 3-5

Magnetorheological materials are prepared by adding a total of 117.9 g carbonyl iron powder (MICROPOWDER-S-1640, GAF Chemicals Corporation) to a corresponding carrier fluid as specified in Table 1. The magnetorheological material is made into a homogeneous mixture through the combined use of low shear and high shear dispersion techniques. Specifically, the particles and carrier fluids are initially mixed by hand, and then more thoroughly dispersed using a high speed disperserator equipped with a 16-tooth rotary head. The weight amount of the iron particles present in each of the magnetorheological materials is equivalent to a volume fraction of 0.30. The magnetorheological materials are stored in polyethylene containers.

Table 1

Example No.	Weight of oil (grams)	Description of Carrier Fluid
3	44.80	83 centipoise, reduced viscosity Poly(methyl-3,3,3-trifluoropropylsiloxane) prepared as described above
4	35.00	50 centipoise [88-92%]-dimethyl / [8-12%]-phenylmethyl-siloxane (PS061, 50 centistoke, Huls America Inc.)
5	64.40	27 centipoise perfluorinated polyether (GALDEN D-10, 12 centistoke, Montedison USA, Inc.)

Mechanical Properties of Examples 3–5

The mechanical properties of the magnetorheological materials prepared in Examples 3–5 are evaluated through the use of parallel plate rheometry. All the magnetorheological materials are observed to exhibit a significant dynamic yield stress at 25°C and magnetic fields of 2000 and 3000 Oersted. These yield stress values are set forth below in Table 2 and are defined as the y-intercept of a linear regression curve fit to the shear stress versus strain rate data obtained from the rheometer.

Table 2

Example	Magnetic Field (Oersted)	Yield Stress (kPa)
3	2000	40.17
3	3000	51.11
4	2000	31.37
4	3000	48.15
5	2000	42.54
5	3000	52.32

As can be seen from the above examples, the magnetorheological materials of the present invention exhibit significant electrorheological activity and are capable of exhibiting stable performance over a temperature range of -40 to 150°C. The consistent performance of the present materials at the diverse temperatures described above is unexpected in light of the highly variable performance of traditional magnetorheological materials under similar diverse temperature conditions.

It is understood that the foregoing is a description of the preferred embodiments of the present invention and that the scope of the invention is not limited to the specific terms and conditions set forth above but is determined by the following claims.

Claims

What is claimed is:

1. A magnetorheological material comprising a carrier fluid and a particle component wherein the carrier fluid has a $\Delta\eta/\Delta T$ ratio less than or equal to about 9.0 centipoise/°C over the temperature range of 25°C to -40°C.

2. A magnetorheological material according to Claim 1 wherein the $\Delta\eta/\Delta T$ ratio is less than or equal to about 7.0 centipoise/°C over the temperature range of 25°C to -40°C.

3. A magnetorheological material according to Claim 1 wherein the carrier fluid is selected from the group consisting of propylene glycol, acetic anhydride, allyl isothiocyanate, benzylacetate, bis(2-butoxy ethyl) ether, bis(2-chloroethyl) ether, bis(2-ethoxyethyl) ether, bis-(2-ethylhexyl)-o-phthalate, bis(2-mercaptoethyl) sulfide, bis(2-methoxyethyl) ether, 1-bromoheptane, 1-bromohexane, 1-bromo-octane, 1,3-butanediol, 2-(2-butoxyethoxy)ethanol, butylbenzene, butylcyclohexane, N-butyldiethanolamine, butyric anhydride, 1-chloro-2-ethylbenzene, 1-chloro-4-ethylbenzene, 1-chloroheptane, 1-chlorooctane, 3-chloropropionitrile, 3-chlorotoluene, cyclohexanone, cyclohexylacetate, cyclooctylamine, decamethyltetrasiloxane, 1-decene, 1,2-dibromobutane, 1,2-dibromo-1,1-dichloroethane, 1,2-dibutoxyethane, dibutyl disulfide, dibutyl maleate, dibutyl sulfide, 2-diethylaminoethanol, 1,4-diethylbenzene, diethyl bromomalonate, diethylsulfide, di-(2-ethylhexyl)-o-phthalate, diethyl malonate, N,N-dimethylbenzylamine, N,N-dimethylformamide, dimethyl malonate, 2,4-dimethylpyridine, dipropyl disulfide, 2-(2-ethoxyethoxy)ethanol, 2-ethoxyethyl acetate, 2-(ethylamino)ethanol, N-ethylaniline, N-ethyldiethanolamine, 2,2'-(ethylenedioxy)bisethanol, ethyl heptanoate, ethyl hexanoate, 2-ethylhexanoic acid, 2-ethyl-1-hexanol, 2-ethylhexyl acetate, ethyl octanoate, S-ethylthioethanol, ethyltoluene, 4-fluoro-1-methoxybenzene, glyceryl tributyrate, heptacosofluoro-tributylamine, heptanal, 1-heptanethiol, hexafluoro-2-phenyl-2-propanol, cis-hexahydroindane, 2,5-hexanediol, hexanenitrile, 1-hexanetriol, 1-hexanol,

hexyl acetate, 2-hydroxyethylhydrazine, 4-hydroxy-4-methyl-2-pentanone, 3-hydroxypropionitrile, indan, 1-iodoheptane, 1-iodopentane, isobutylbenzene, isopropylbenzene, isopropylcyclohexane, isopropyl-1-methylbenzene, limonene, 3-methoxy-1-butanol, 2-(2-methoxyethoxy)ethanol, methyl acetoacetate, N-methylaniline, methylcyclopentadiene dimer, methyl heptanoate, methyl hexanoate, 1-methylimidazole, 4-methylpentanenitrile, 2-methylpentanoic acid, 2-methylpropionic acid, 1-nitrobutane, 2-nitroethanol, nonane, nonanoyl chloride, octanenitrile, 1-octanethiol, octanoyl chloride, 1,5-pentanediamine, pentyl acetate, 1-phenylhexane, pinane, pinene, 1,2,3-propanetriol triacetate, cis-propenylbenzene, propionic anhydride, propylcyclohexane, propyl benzoate, squalene, tetraethylgermanium, tetraethyltin, tetrahydropyran-2-methanol, 2,6,10,14-tetramethylpentadecane, tributylamine, tributyl borate, tributyl phosphate, 1,3,5-trimethylbenzene, 2,6,8-trimethyl-4-nonanone, trimethylphospate, 1,2,4-trimethylpiperazine, tripropylamine, 1-undecene, and mixtures thereof, as well as mixtures of propylene glycol and ethylene glycol with water wherein the ratio of alkylene glycol to water is between 60:40 to 95:5.

4. A magnetorheological material according to Claim 1 wherein the carrier fluid is a polysiloxane or perfluorinated polyether and has a viscosity between about 3 and 200 centipoise at 25°C.

5. A magnetorheological material according to Claim 4 wherein the carrier fluid has a viscosity between about 5 and 100 centipoise at 25°C.

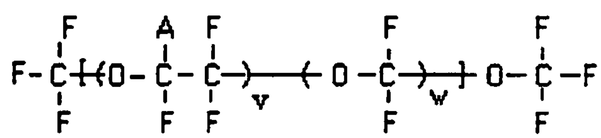
6. A magnetorheological material according to Claim 4 wherein the polysiloxane is a silicone homopolymer or copolymer comprising a siloxane polymeric backbone substituted with hydrocarbon radicals as side and end groups, wherein the hydrocarbon radicals can be either straight chain, branched or cyclic, as well as aliphatic or aromatic with the number of carbon atoms ranging from 1 to about 8 and wherein the hydrocarbon radicals may contain H, N, O, S, Cl, Br or F functionality.

7. A magnetorheological material according to Claim 6 wherein the polysiloxane is selected from the group consisting of polydimethylsiloxanes, polymethylphenylsiloxanes, poly(methyl-3,3,3-trifluoropropyl)siloxanes, polychlorophenylmethylsiloxanes, dimethyl-(tetrachlorophenyl)siloxane copolymers, dimethyl(phenylmethyl)-siloxane copolymers, dimethyl(diphenyl)siloxane copolymers, and methyl-3,3,3-trifluoropropyl(dimethyl)siloxane copolymers.

8. A magnetorheological material according to Claim 7 wherein the polysiloxane is a polydimethylsiloxane.

9. A magnetorheological material according to Claim 4 wherein the perfluorinated polyether is a linear fluorinated polymer containing a polyether backbone consisting of carbon and oxygen atoms with either CF_3 or F functionality.

10. A magnetorheological material according to Claim 9 wherein the perfluorinated polyether corresponds to the following formula:



wherein A can be F or CF_3 and the ratio of v/w is between about 30 and 50.

11. A magnetorheological material according to Claim 10 wherein the ratio of v/w is between about 35 and 45.

12. A magnetorheological material according to Claim 1 wherein the particle component is comprised of a paramagnetic, superparamagnetic or ferromagnetic compound.

13. A magnetorheological material according to Claim 12 wherein the particle component is comprised of a material selected from the group consisting of iron, iron alloys, iron oxide, iron nitride, iron carbide, carbonyl iron, chromium dioxide, low carbon steel, silicon steel, nickel, cobalt, and mixtures thereof.

14. A magnetorheological material according to Claim 1 wherein the particle component is a metal powder selected from the group consisting of straight iron powders, reduced iron powders, insulated reduced iron powders, and cobalt powders.

15. A magnetorheological material according to Claim 1 wherein the particle is a straight iron powder, a reduced iron powder, an iron oxide powder/straight iron powder mixture or an iron oxide powder/reduced iron powder mixture.

16. A magnetorheological material according to Claim 1 further comprising a surfactant.

17. A magnetorheological material according to Claim 16 wherein the surfactant is selected from the group consisting of ferrous oleate and naphthenate, aluminium soaps, alkaline soaps, sulfonates, phosphate esters, stearic acid, glycerol monooleate, sorbitan sesquioleate, stearates, laurates, fatty acids, fatty alcohols, fluoroaliphatic polymeric esters, hydrophobic fumed silica, precipitated silica gel, and titanate, aluminate or zirconate coupling agents.

18. A magnetorheological material according to Claim 17 wherein the surfactant is hydrophobic fumed silica, precipitated silica gel, a phosphate ester, a fluoroaliphatic polymeric ester or a coupling agent.

19. A magnetorheological material according to Claim 18 wherein the precipitated silica gel is dried in a convection oven at a temperature from about 110°C to 150°C for a period of time from about 3 to 24 hours.

20. A magnetorheological material according to Claim 1 wherein particle settling is minimized by the formation of a thixotropic network.

21. A magnetorheological material according to Claim 1 wherein the carrier fluid is present in an amount ranging from about 50 to 95 percent by volume and the particle component is present in an

amount ranging from about 5 to 50 percent by volume of the total magnetorheological material.

22. A magnetorheological material according to Claim 21 wherein the carrier fluid is present in an amount ranging from about 60 to 85 percent by volume and the particle component is present in an amount ranging from about 15 to 40 percent by volume.

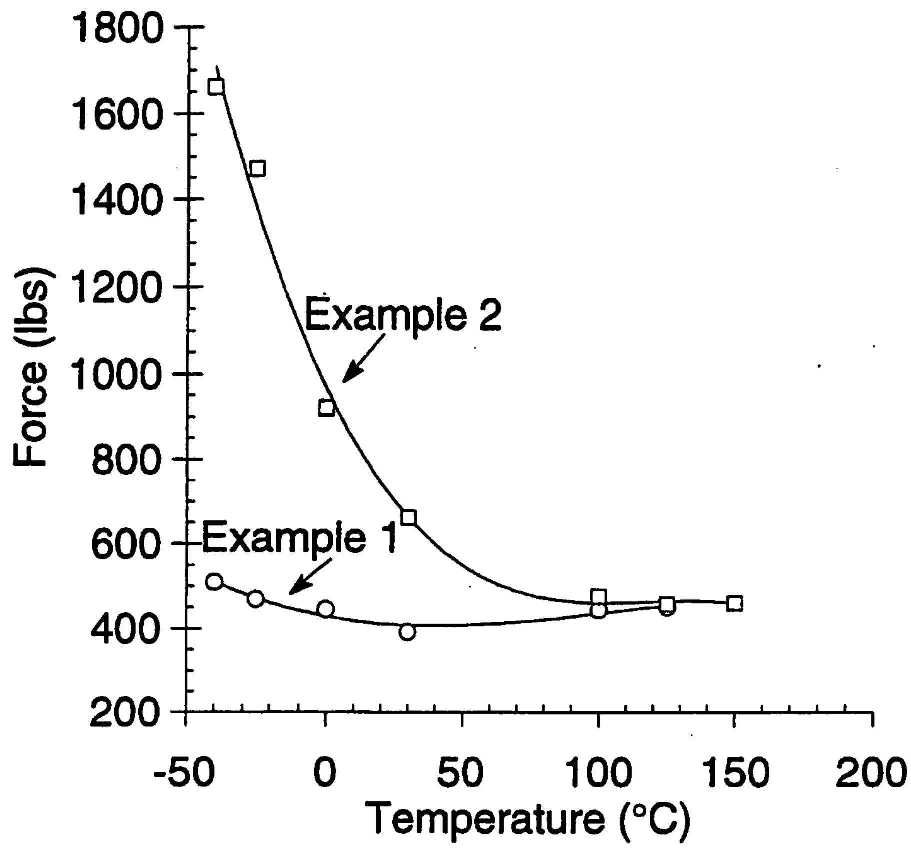

Force (lbs)
1800
1600
1400
1200
1000
800
600
400
200
Example 2
Example 1
-50
0
50
100
150
200
Temperature (°C)

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/09735

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :H01F 1/28
US CL :252/62.52, 62.54, 62.55, 62.56
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/62.52, 62.54, 62.55, 62.56

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,356,098 (Chagnon) 26 October 1982. See col. 2, lines 28-38; the paragraph bridging cols. 3 and 4; the paragraph bridging cols. 4 and 5; col. 5, lines 4-13; and Example 3.	1-2, 4-13, 16 and 20-22
X	US, A, 4,976,883 (Kanno et al.) 11 December 1990. See col. 2, line 6 - col. 3, line 9; col. 3, lines 14-17; col. 4, lines 21-25; and claim 5 at col. 7	1-3, 12-13 and 16-22
X	AU, A, 162,371 (Bataafsche) 23 October 1952. See page 2, line 28 - page 3, line 20; page 4, lines 15-22; page 5, lines 11-29 and 33-39; and page 6, lines 1-13.	1-22

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search: 17 NOVEMBER 1993

Date of mailing of the international search report: 27 DEC 1993

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/09735

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,917,538 (Rosensweig) 04 November 1975. See col. 3, line 60 - col. 4, line 59.	1-2 and 4-22
Y	US, A, 5,007,513 (Carlson) 16 April 1991. See col. 5, line 56 - col. 6, line 10.	1-11